Gas Phase γ-Radiolysis of n-Butane and n-Pentane in the Presence of Tetracarbonyl Nickel

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$Ni(CO)_4$ reacts with ionic species produced by the γ-radiolysis of n-butane and n-pentane modifying ion-molecule reaction paths. The major effect is a tenfold increase of the ethylene yield and a loss of other light products. The effect of ionic and radical reactions with $Ni(CO)_4$ is briefly discussed.

Introduction

[60]Co γ-radiolysis of simple alkanes in the gas phase has been widely investigated with the aim of elucidating the relative contribution of ionic, radical and molecular decomposition processes. To this purpose the effect of phase, density and temperature have been studied with the aid of radicals, ions and electrons scavengers [1–5].

We recently reported that added volatile metal carbonyls such as $Ni(CO)_4$ and $Fe(CO)_5$ sharply affect the yield of final stable products in the reactions of recoil T with simple hydrocarbons and silanes [6–8]. It has been suggested that metal carbonyls interact with thermal species (radicals) modifying their reaction paths to final products.

Radiolysis experiments on mixtures of n-butane and $Ni(CO)_4$ were devised to obtain insight on the interactions of metal carbonyls with radiolytically produced reactive species [7].

Experiments on the γ-radiolysis of pure $Ni(CO)_4$ showed considerable radiation stability for this compound [9], probably due to the thermal back reaction (1) observed in flash photolysis [10]:

$$Ni(CO)_4 \rightleftharpoons Ni(CO)_3 + CO \qquad (1)$$
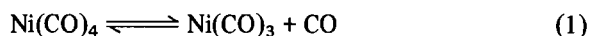
Moreover, $Ni(CO)_4$ appears to develop a protective effect on the radiolytical decomposition of benzene and cyclohexane, probably because of its low ionization potential [11].

In this paper we report some findings on the effect of $Ni(CO)_4$ on the radiolysis of n-butane and n-pentane in the gas phase.

Experimental

n-Butane ≥99.5% (Rivoira Co.) and $Ni(CO)_4$ (Stream Chemical Inc.) were subjected to several freezing-pumping cycles before use. n-Pentane ≥99.4% (C. Erba) was dried over silica-gel and deoxygenated by saturation with Argon. n-Butane and n-pentane samples were sealed in Pyrex ampoules (10 cm³ vol.) at a pressure of 8.0×10^4 and 6.5×10^4 Pa respectively, alone or with 10% $Ni(CO)_4$.

The samples were radiolyzed with [60]Co γ-rays at a dose rate of 2.7 Gy sec^{-1} (~1 Mrad h^{-1}) for 80 hours, using the γ-irradiation facility of Gammatom Co. (Guanzate). The dose rate was checked by Fricke dosimetry and the total dose calculated from dose rate and irradiation time.

The analysis of the irradiated samples was performed by gas-chromatography using a 2.5 m × 6 mm i.d. glass column of Chromosorb 105 (J. Manville) 60/80 mesh. The gas-chromatograph (C. Erba mod. 4200) was equipped with F.I.D.

Some sample from recoil T experiments, prepared with large amount of ³He [12] and bombarded with very high neutron dose to increase the radiation damage to the system, were analyzed by F.I.D. after radio-gas-chromatography [6, 7].

Results

The results obtained from the γ-radiolysis of n-butane are reported in Table I, as yields per 100 eV of absorbed energy. Some literature data are reported on the same Table for comparison.

Table II shows the G values for some of the products obtained from the γ-radiolysis of gaseous n-pentane. For comparison some yields from Futrell [13] are also reported.

TABLE I. G. Values for γ-Radiolysis of Gas-Phase n-Butane.

Additives Products	This work[a] −	This work[a] Ni(CO)$_4$	Miyazaki[b] −	Miyazaki *et al.*[c] −
CH$_4$	1.95	1.83	4.21	0.96
C$_2$H$_2$	0.12	−	−	−
C$_2$H$_4$	0.22	2.52	1.56	0.59
C$_2$H$_6$	3.96	2.46	2.88	1.89
C$_3$	4.12	3.21	2.43	2.30

[a]Pressure 8.0 × 10^4 Pa. T = ~ 300 K. Dose rate 2.7 Gy sec^{-1} ^{60}Co. Totale dose 80 × 10^4 Gy.   [b]Pressure 1.0 × 10^5 Pa. T = 423 K. Dose rate 0.24 Gy sec^{-1} ^{137}Cs. Total dose 2.06 × 10^4 Gy [5].   [c]Pressure 1 × 10^4 Pa. T = 293 K. Total dose 40 × 10^4 Gy (electrons) [3].

TABLE II. G Values for γ-Radiolysis of Gas-Phase n-Pentane.

Additive Products	This work[a] −	This work[a] Ni(CO)$_4$	Futrell[b] −
CH$_4$	1.41	1.18	0.7
C$_2$H$_2$	0.07	−	0.5
C$_2$H$_4$	0.25	2.37	1.5
C$_2$H$_6$	4.11	2.12	1.1
C$_3$	5.83	4.40	2.0
C$_4$	1.55	1.35	0.4

[a]Pressure 6.5 × 10^4 Pa. Temperature = ~300 K. Dose rate 2.7 Gy sec^{-1} ^{60}Co. Total dose 40 × 10^4 Gy.   [b]^{60}Co irradiation conditions not reported [13].

The G values obtained in our experiments are not easily comparable with those reported in the literature, because of large differences in experimental conditions.

Experimental variables such as temperature, pressure, dose rate and total dose have been showed to affect G values [3–5]. In particular the G(ethylene) to G(ethane) ratio decreases as the dose increases [14] and as the density of the gas decreases [5].
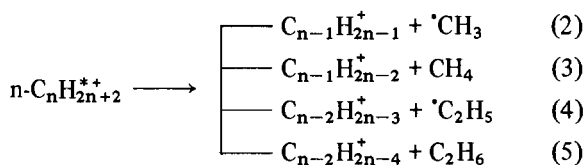
Discussion

During the γ-radiolysis of alkanes a large spectrum of excited ions, excited molecules and radicals is formed. According to the literature [2, 4] the decomposition of highly excited ions and the subsequent ionic reactions play a primary role in low pressure experiments, wheras radical and molecular processes increase their importance in high pressure and liquid phase experiments.

In gas phase the decomposition of the highly excited n-butane ions may be as outlined in Scheme 1.
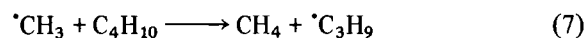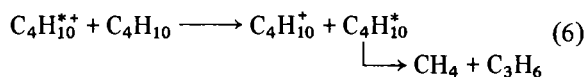
From the reactions of the species reported on the Scheme all the observed products could be derived.

Scheme 1.

$$n\text{-}C_nH_{2n+2}^{*+} \longrightarrow \begin{cases} C_{n-1}H_{2n-1}^+ + {}^{\cdot}CH_3 & (2) \\ C_{n-1}H_{2n-2}^+ + CH_4 & (3) \\ C_{n-2}H_{2n-3}^+ + {}^{\cdot}C_2H_5 & (4) \\ C_{n-2}H_{2n-4}^+ + C_2H_6 & (5) \end{cases}$$

n-Butane

According to the literature [2, 4] methane could be formed through reactions (3), (6) and (7):

$$C_4H_{10}^{*+} + C_4H_{10} \longrightarrow C_4H_{10}^+ + C_4H_{10}^* \qquad (6)$$
$$\longrightarrow CH_4 + C_3H_6$$

$${}^{\cdot}CH_3 + C_4H_{10} \longrightarrow CH_4 + {}^{\cdot}C_3H_9 \qquad (7)$$

Experiments with mixtures of C$_4$H$_{10}$ and C$_4$D$_{10}$ demonstrated that molecular eliminations (3) and (6) are the main source of methane [2], while using I$_2$ as scavenger the reaction (7) has been shown to be unimportant [3].

Possible sources of ethylene are: the elimination of H$^{\cdot}$ from excited ethyl radicals, the decomposition of excited butane molecules [2] and hydride transfer reaction from n-butane and vinyl ions (8) originating from the decomposition of ethyl (and propyl) ions [2]

$$C_2H_3^+ + C_4H_{10} \longrightarrow C_2H_4 + C_4H_9^+ \qquad (8)$$
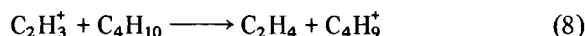
Ethane is formed by molecular elimination reaction (5) and by hydride transfer reaction (9)

$$C_2H_5^+ + C_4H_{10} \longrightarrow C_2H_6 + C_4H_9^+ \qquad (9)$$
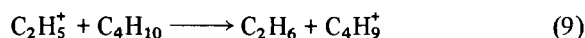
Hydrogen abstraction by ethyl radicals and decomposition of excited butane molecules could also be considered as sources of ethane production. According to Ansloos however [2] reaction (5) and (9) are the main routes for the formation of C$_2$H$_6$.

Propane and propylene are produced by hydride transfer reactions to C$_3$ ions, formed according to reactions (2), (3) and (10) [2]

$$C_3H_7^+ \longrightarrow C_3H_5^+ + H_2 \qquad (10)$$

Contributions from radical reactions and unimolecular decomposition, though possible, have not been considered.

$Ni(CO)_4$ has been shown to act as an energy sink in radiolysis of cyclic hydrocarbons [11]. The change in the product yield of the radiolysis when the carbonyl is present could then be attributed to some kind of protective effect on the hydrocarbon. Alternatively, the total products yield being unaffected by the metal carbonyl, the change in the single product yield could be attributed to an interference of $Ni(CO)_4$ on the reaction sequence outlined above.

In mass spectrometry, metal carbonyls are known to react with alkyl ions to give ionic intermediates [15]. Alkanes also react with metal ions and metal–CO ions to give ionic intermediates [16] containing metal–carbon bonds.

In such ionic complexes the organic part appears to rearrange to olefinic structure, as shown by the mass spectrum of the ionic species.

Thus the alkyl ions produced by radiolysis may be assumed to react with $Ni(CO)_4$ and/or some of its decomposition products, to be neutralized to molecules or radicals, or to give rise to intermediate ionic complexes which are responsible for the change in the yield of the products.

A reaction with the primary alkyl ions, such as $C_4H_{10}^{*+}$ and $Ni(CO)_4$, is not likely because of the high decomposition rate of the ion ($\sim 2 \times 10^{11}$ sec^{-1}) and the low collision frequency with the surrounding species. It is more reasonable to assume an interaction of the metal carbonyl with ionic species formed from the decomposition of $C_4H_{10}^{*+}$, or with $C_4H_{10}^{*+}$ bearing less than 8×10^{-9} J of excitation energy. As outlined above, the major effect of the added carbonyl is the tremendous increase in the yield of ethylene and the decrease in both ethane and C_3 hydrocarbons.

The decrease in ethane yield may be attributed to the reaction between $C_2H_5^+$ and $Ni(CO)_4$ (11), leading to ethylene in competition with the hydride transfer reaction (9) which produces ethane. This reaction has been observed in mass spectrometry [17].

$$C_2H_5^+ + Ni(CO)_4 \longrightarrow C_2H_4 + Ni(CO)_4H^+ \qquad (11)$$
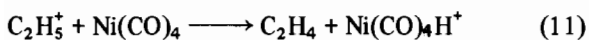
A similar reaction of $C_3H_7^+$ with $Fe(CO)_5$, leading to C_3H_6 and $Fe(CO)_5H^+$, has been reported by Ridge [15] and its reaction rate is of the same order of magnitude as the hydride transfer reaction from C_4H_{10} to $C_3H_7^+$ [18]. According to Munson [18] the $C_2H_5^+$ ion reacts with butane faster than does $C_3H_7^+$. It could then be supposed that it reacts with $Ni(CO)_4$ faster than with $Fe(CO)_5$. On the other hand $Ni(CO)^+$ is more reactive with hydrocarbons than is $Fe(CO)^+$ [16]. Reaction (11) is then likely to occur and, in agreement with the decrease of the C_2H_6 yield, its rate should be at least equal to the rate of reaction
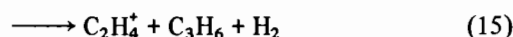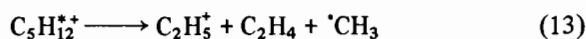
(9). The reaction between $Ni(CO)_4$ and $C_4H_{10}^{*+}$, carrying an excitation energy $\leqslant 8 \times 10^{-19}$ J ($\leqslant 5$eV) (12), competes with reaction (3) causing the increase of ethylene and the decrease of C_3 and CH_4.

$$C_4H_{10}^{*+} + Ni(CO)_4 \longrightarrow 2C_2H_4 + Ni\text{-complex} \qquad (12)$$
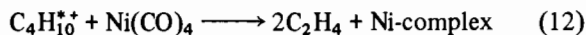
Reaction (12) has not been studied by mass spectrometry but appears reasonable both from experimental evidence and from the bond cleavage and dehydrogenating properties of Ni complexes [19].

n-Pentane

Radiolysis of gas-phase n-pentane follows the same reaction sequence as outlined in Scheme 1, with the addition of reactions (13), (14) and (15) as alternative sources for methane, ethylene, ethane and C_3 hydrocarbons [20]

$$C_5H_{12}^{*+} \longrightarrow C_2H_5^+ + C_2H_4 + {}^\bullet CH_3 \qquad (13)$$
$$\longrightarrow C_2H_4^+ + C_3H_8 \qquad (14)$$
$$\longrightarrow C_2H_4^+ + C_3H_6 + H_2 \qquad (15)$$

Though the secondary products spectrum is qualitatively similar to that of butane, it differs for the amount of each species and for the energy distribution.

As for butane the presence of $Ni(CO)_4$ reduces the yields of fragmentation products, with the exception of ethylene. However the mass balance for fragmentation products is not so satisfactory as for butane, *i.e.* there is no balance between the increase of C_2H_4 and the decrease of ethane and C_3. This fact could be attributed to the absence, in the pentane system, of butane ions in low excitation state, whose reaction with $Ni(CO)_4$ was supposed to contribute to the depletion of C_3 and to the increase of C_2H_4. Furthermore, under the same energy conditions the decomposition rate of excited pentane ions is about 50 times lower than that for butane species, so that the neutralization deactivation reaction with $Ni(CO)_4$ (16) is allowed.

$$C_5H_{12}^{*+} + Ni(CO)_4 \longrightarrow C_5H_{12} + \text{products} \qquad (16)$$

According to reaction (16), $Ni(CO)_4$ acts as an energy sink (11) decreasing the probability of decomposition to ethylene, C_3 and C_4.

Ionic and Radical Processes

Despite the apparently similar behaviour of $Ni(CO)_4$ towards the ethylene yield, the results obtained in alkane radiolysis seem to be in contrast with previous results on recoil T chemistry [6, 7]. In γ-radiolysis the addition of $Ni(CO)_4$ causes a general decrease of the fragmentation products (with the exception of ethylene), while a general increase in T-labelled fragmentation products has been observed in $T^* +$ alkane systems [6, 7].

It should be pointed out that in hot atom chemistry the secondary products (*i.e.* products not arising from hot substitution or abstraction reactions) are universally accepted to be due to labelled radicals reactions with substrate [21]. On the contrary in gas-phase radiolysis the final products are largely formed by ion-molecule reactions, radical reactions being a minor process. The differences observed experimentally in the two cases can then be ascribed to a different behaviour of both ionic and radical species towards the metal carbonyl.

Radical reactions could be evidence of radical plus ionic reactions if labelled radicals (from recoil T reactions) are used to trace radical processes and labelled products detected by radiochemical methods (radio gas-chromatography). F.I.D. could then be used to detect the total products yield, *i.e.* from both radical and ionic reactions.

TABLE III. Effects of Radical and Overall Processes for Radiolysis of C_4H_{10} and $Ni(CO)_4$ Mixture.

Single products yield ratio	$\dfrac{T^* + C_4H_{10} + Ni(CO)_4}{T^* + C_4H_{10}}$	
labelled products[a] (from radicals)	total products[b] (from ions)	
CH_4	2.6	0.97
C_2H_4	4.5	11.0
C_2H_6	1.6	0.61
C_3	1.7	0.77

[a] Detected by radiation measurement. [b] Detected by mass measurement: F.I.D.

Table III shows how much the yield of each reaction products is affected by ionic and/or radical processes. The first column shows that radical reactions with $Ni(CO)_4$ induce some new radical process which increases the yield of fragmentation products accordingly to the mechanism already reported [6–8]. The second column shows that, agreeing with the above discussion, the reactions of ionic species

with $Ni(CO)_4$ cause a pronounced increase in ethylene and a sharp decrease in the other fragmentation products. Only the particularly high sensitivity of the radioactivity detector allowed us to trace the radical processes with $Ni(CO)_4$, because ionic processes are in such large amounts as to overwhelm the effect of the reaction of the carbonyl with radicals.

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